

SiOH-Functionalized Polystyrene Latexes. A Step toward the Synthesis of Hollow Silica Nanoparticles

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Following a previous work (Tissot, I.; Lefebvre, F.; Bourgeat-Lami, E. *Macromolecules* **2001**, submitted for publication), polystyrene latex particles containing silanol groups have been synthesized in emulsion polymerization using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional comonomer. The surface properties of the functionalized polymer latexes were investigated in depth using electrophoretic measurements and the soap titration method. Both techniques gave qualitative evidence of the presence of SiOH groups at the particles surface. The concentration of surface charges was quantified by potentiometric and conductometric titrations. As expected, the surface charge density increased with an increase in the pH and with an increase in the MPS concentration. Because of the presence of silanol groups at the particles surface, no loss of colloidal stability was observed when the functional polystyrene latexes were suspended into ethanol/water mixtures. The silanol groups were then converted into a 20 nm thick silica layer using a procedure derived from the Stöber method (Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62). Hollow silica nanoparticles were finally generated by thermal degradation of the templating organic latex core. This work illustrates the determining role of interfaces in the structuration of organic–inorganic colloids.

Introduction

If one tries to answer the question of why there are so many scientists excited by the nanostructuring of materials, a response could be that the manipulation of chemical and macromolecular structures at the nanoscale is still a technological and scientific challenge.³ An emerging discipline in this field is that of organic–inorganic materials which can be tailor-made with an infinite number of architectures and in diverse forms (monoliths, thin films, fibers, powders, or particles).⁴ To this end, colloidal science obviously offers versatile routes to control the bulk composition, size, shape, and surface properties of nano-objects. For that reason, heterophase polymerizations (i.e., emulsion, miniemulsion, dispersion, and suspension polymerizations) have been largely developed in the last 10 years to synthesize organic–inorganic colloidal nanocomposites.⁵

The design and synthesis of nanoscale objects require a good deal of control over interfaces in order to build

up and organize the nanostructures.⁶ A typical example is that of polymer encapsulation of pigments and fillers.^{7–10} Specific groups are introduced, for instance, onto minerals to increase the chemical affinity with the shell material. Caris⁷ and Corcos⁸ used titanate and silane coupling agents to encapsulate titanium dioxide and silica particles, respectively. Armes et al. described the synthesis of polymer/silica nanocomposites and used 4-vinylpyridine to generate strong acid–base interactions.⁹ Caruso et al. reported the consecutive assembly of silica nanoparticles and polymers onto colloidal templates by means of electrostatic interactions.¹⁰ A chemically anchored transfer agent initiator was used by Patten to conduct living free-radical polymerization of styrene and methyl methacrylate monomers from the surface of inorganic seed particles.¹¹ Fleming involved specific chemical and biochemical interactions to control the assembly of polystyrene nanoparticles onto silica microspheres.¹² It turns out from the aforementioned works that controlling the surface properties of the core particles is essential if we want to obtain organic–

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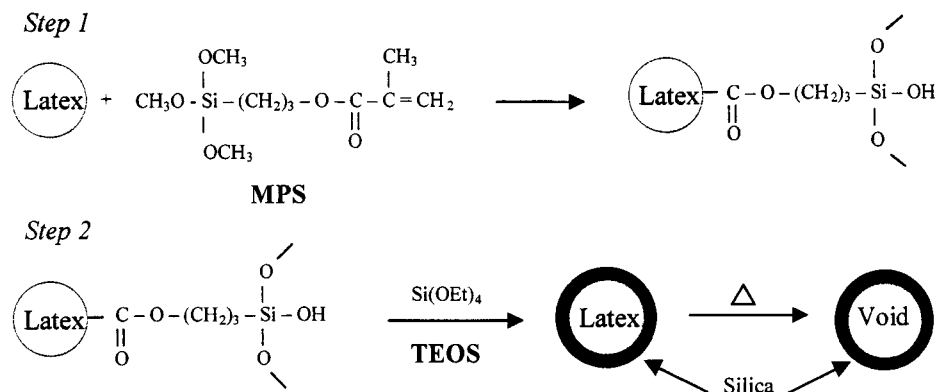
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Scheme 1. Schematic Representation of the Different Steps Involved in the Coating Reaction of SiOH-Functionalized Latex Particles with Silica and the Formation of Hollow Silica Beads



inorganic colloids with specific morphology (i.e., core-shell, hairy, raspberry-like, etc.).

Surface modification of minerals and polymers can be done in two steps by first synthesizing the nanoparticles and subsequently treating them with a convenient coupling agent molecule. Many examples of this type can be found in chromatography and in biotechnologies.^{13–16} However, the incorporation of specific groups can also be performed directly during polymerization using convenient functional monomers, for instance, cationic,¹⁷ zwitterionic, or monomers bearing specific chemical functions (e.g., aldehydes, amines, acids, bases, etc.).^{18–20} In the present paper, we report our results on the incorporation of silanol groups into polystyrene latex particles using 3-(trimethoxysilyl)propyl methacrylate (MPS) as a functional comonomer. Our preliminary investigations in that field have been presented in a previous paper.¹ The experimental conditions leading to stable colloidal suspensions were reported in that paper along with the results of an analysis of the structure of the copolymers by NMR and infrared spectroscopy. In the current work, we report more details on the surface properties of the functionalized latex particles and on the formation of a silica layer at the polymer particle surface through hydrolysis and condensation of tetraethoxysilane (TEOS) in aqueous ammoniacal alcoholic suspensions. Hollow silica nanoparticles were obtained in a subsequent step by thermal degradation of the polymeric latex core as depicted in Scheme 1.

To the best of our knowledge and despite the large number of papers which have already been published in that field,²¹ the idea of incorporating silanol groups onto polymer particles to provide chemical functions for

subsequent coating with silica has never been investigated. Liz-Marzan and coauthors described the surface complexation of gold nanoparticles by a silane coupling agent, (3-aminopropyl)trimethoxysilane, to render the gold vitreophilic and compatible with a silica layer.^{22,23} Using a similar strategy, Mann et al. grew organosilica shells with tailored functionalities on gold surfaces.²⁴ Philipse and co-workers described the use of “active” silica and the subsequent growth reaction of tetraalkoxysilane on boehmite core nanorods²⁵ and magnetite.²⁶ Similarly, silica-coated zinc sulfide (ZnS)²⁷ or hematite (α -Fe₂O₃)²⁸ particles were synthesized using a seeded-growth technique derived from the Stöber method. However, none of these studies concern polymer latexes. Strategies for coating of polymers with minerals mostly involve electrostatic interactions. For instance, spherical particles of yttrium compounds were obtained by the controlled precipitation from solution of yttrium nitrate in the presence of urea and poly(vinylpyrrolidone).^{29,30} Titania-coated polymer latexes have been prepared in one step by the hydrolysis of a titanium alkoxide in the presence of cationic polystyrene particles.³¹ The positive charge of the surface ensures a rapid capture of the highly reactive titania species without the formation of any secondary titanium dioxide particles. Finally, Caruso reported the layer-by-layer self-assembly of polyelectrolytes and silica nanoparticles onto polymer latexes of opposite charge.¹⁰ The key point in all of these works is the need for significant chemical or physicochemical interactions between the core and shell materials.

In the following, we want to report a novel, complementary approach along these same lines on the use of a coupling agent to covalently attach silanol groups at the surface of polystyrene latex particles for compati-

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bilization with a silica shell. Not only does this approach provide a versatile route to the design of silica-coated polymer latexes and hollow silica spheres, but it can also be combined with already existing coating procedures (of, e.g., minerals with polymers)^{8,32} to obtain multi-composite systems composed of alternate organic-inorganic layers or made of several organic-inorganic core-shell nanoparticles encapsulated into polymer microspheres.

Experimental Section

Materials. The monomer, styrene (Aldrich), was distilled in a vacuum before use. The initiator, potassium persulfate (KPS, Acros Organics), and the surfactant, dodecyl dimethyl-propylammonium sulfonate (Ralufon, Aldrich), were used as supplied. MPS (Aldrich) and TEOS (Acros) were used without purification. The water was deionized on mixed-bed resins. Ethanol containing 5 wt % of water was supplied by Laurylab.

Synthesis of the SiOH-Functionalized Polystyrene Latex Particles and Coating with Silica. *SiOH-Functionalized Polystyrene Latexes.* According to the results of our previous work in this area,¹ the SiOH-functionalized latex particles were prepared in two steps. Emulsion polymerization of styrene was first carried out at 70 °C up to 80% conversion using KPS as the initiator and Ralufon as the surfactant. Once 80% conversion was achieved, known amounts of MPS were added to the reaction medium and the polymerization was continued at 70 °C for 5 h. The pH of the suspension was fixed at pH = 7 by adding equivalent quantities of dihydrogenophosphate and dihydrogenocarbonate (typically 0.1 g of each per 100 g of water). A typical recipe is as follows: styrene 10 g, KPS 0.1 g, Ralufon 0.2 g, buffer 0.2 g, water 100 g, and various quantities of MPS (0.5, 1, 2, and 4 g).

Coating of the SiOH-Functionalized Latex Particles with Silica. In a typical experiment, 1 g of the functional polystyrene latex particles was suspended in 100 g of a 95/5 ethanol/water mixture containing 0.4 mol/L ammonium hydroxide. Exchange of solvent was performed by dialysis using cellulose tubing (Membra Cell, Polylabo). A total of 15 g of TEOS dissolved in 15 g of ethanol was then added dropwise to the hydroalcoholic ammoniacal suspension under magnetic stirring at room temperature at a rate of 1 mL/h.

Hollow Silica Nanoparticles. The silica-coated latex particles were dried at 70 °C to evaporate the water, and the powder thus obtained was heated at 600 °C under air for 4 h to produce hollow silica spheres. The calcinated product was suspended in water with the aid of ultrasound.

Characterization of the SiOH-Functionalized Latex Particles. *Particles Size and Morphology.* The diameter of the latex particles, D_p , was determined by dynamic light scattering (DLS) using a Malvern Autosizer Lo-C. Transmission electron microscopy (TEM) analysis was used to characterize the particle morphology. In a typical experiment, 1 drop of the colloidal dispersion was put on a carbon film supported by a copper grid, allowed to dry in air, and then observed using a Philips CM10 electron microscope operating at 80 kV.

ζ Potential Measurements. The electrophoretic mobility was determined using a laser electrophoresis ζ potential analyzer (Zetasizer III from Malvern instruments). The analyses were carried out at 20 °C, and the ζ potential was an average of three measurements. The ionic strength was kept constant by dilution into a 0.001 mol/L sodium chloride solution. The pH of the suspension was controlled by adding 0.1 N standard hydrochloric acid or sodium hydroxide aqueous solutions. The ζ potential was calculated from the electrophoretic mobility (μ), using the Smoluchowsky equation.³³

Point of Zero Charge (PZC). The PZC was evaluated by chemical titration using a glass electrode (Beckman, type E) and measuring the pH of the suspension after successive additions of a standard 0.01 N hydrochloric acid solution for two different electrolyte concentrations (10^{-3} and 10^{-1} M NaCl, respectively). The PZC was identified graphically by plotting Δ pH as a function of pH and determining the point at which Δ pH is equal to zero.³³

Surface Charge Density Measurements (σ_0). The surface charge density, σ_0 , was determined using either potentiometric or conductometric titrations. The conductivity was recorded using a CDM 80 conductivity meter, and the pH was determined using a glass electrode (Beckmann, type E). To obtain reliable data, all of the titrations were performed under a nitrogen atmosphere on a constant volume of the latex suspension (100 mL) containing 1 g of solid. A known volume of 0.01 N hydrochloric acid (typically around 5 mL) was added to the suspension in order to reach the PZC. The pH of the suspension was then increased from the PZC to pH = 10.7 by the addition of known quantities of a 0.01 N sodium hydroxide solution. After each addition of NaOH, the pH or the conductance was used to determine the concentration of the OH⁻ ions in the medium. The charge density was calculated from the difference between the amount of OH⁻ added and that remaining in solution after titration. In both cases, blank titration experiments were performed under rigorously identical conditions in order to establish the relation between the pH or the conductance and the OH⁻ ions concentration. The surface charge density was calculated from the latex solid contents and the titration data.

Soap Titration Method. The occupied area per SDS molecule onto the functional latexes at the saturation adsorption (A_m) was determined from soap titration following the method developed by Maron.³⁴ The number of SDS molecules needed to saturate the latex particles surface was obtained by the difference between the critical micellar concentration (cmc) of SDS determined in the latex suspension and that in the water.

Porosity Measurements. Nitrogen adsorption measurements were performed on the cleaned powder after degassing at 70 °C under vacuum. The Brunauer-Emmett-Teller (BET) method was applied to the nitrogen adsorption isotherm curves to determine the specific surface area and the pore volume of the latex particles.³⁵ The pore size was calculated from the desorption isotherm curves using the Brunauer-Joyner-Halenda (BJH) method. The pore radius (R_p) was obtained by assuming cylindrical pores.³⁶

Results and Discussion

Synthesis and Characterization of SiOH-Functionalized Polystyrene Latex Particles. The influence of the MPS concentration on the particle size, composition, and surface properties was examined using various experimental techniques. For this purpose, a series of functional polystyrene latexes containing different amounts of MPS (from 5 to 40 wt % relative to styrene) were synthesized under the same experimental conditions.

Particle Size and Chemical Composition. The diameters and the chemical composition of the SiOH-functionalized latex particles after removal of nonreacted MPS and free surfactant are given in Table 1 for different MPS concentrations. As expected, the particle size increases with increasing amounts of MPS. On the other hand, gravimetric analysis indicates almost complete monomer conversion whatever the MPS concen-

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Table 1. Particle Size and Chemical Analysis of the SiOH-Functionalized Latex Particles as a Function of the MPS Concentration

	runs				
	0	1	2	3	4
[MPS] in the feed (wt % to styrene)	0	5.5	11	20.8	40.4
particle size (D_p , nm)	120	126	135	139	152
conversion (%)	100	98.4	98.1	98.1	98.8
elemental analysis					
C (%) ^a	91.1	89.75	87.55	84.3	79.4
Si (%) ^a	0	0.60	1.13	1.88	3.15
copolymer composition					
MPS (%) ^a	0	5.15	9.7	16.14	27.04
styrene (%) ^a	98.7	94.8	90.28	83.74	73.31
MPS (wt % to styrene)	0	5.4	10.7	19.3	36.9

^a In grams per 100 g of dried powder.

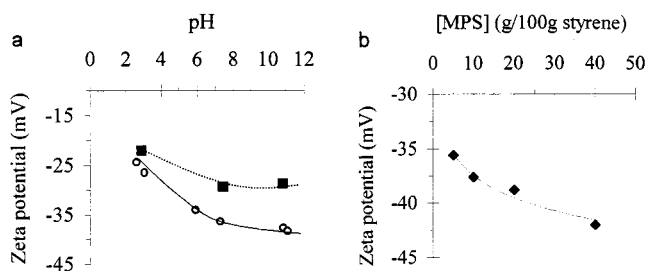


Figure 1. (a) Variation of the ζ potential as a function of pH (NaCl, 10^{-3} M; ■, pure polystyrene latex particles; ○, 10 wt % MPS-functionalized latex particles). (b) Variation of the ζ potential as a function of the MPS concentration (NaCl, 10^{-3} M; pH = 11).

tration. Quantitative incorporation of MPS into the polystyrene latex particles was also confirmed by carbon and silicon elemental analyses, which indicate that the copolymer composition is quite close to the (co)monomer feed ratios (Table 1). Those results are consistent with the spectroscopic analysis reported in our preliminary work and are due to the high reactivity of the silane molecule in the copolymerization reaction.

ζ Potential Measurements. Electrophoresis is a convenient method to characterize the surface properties of polymer and metal oxide colloids. The evolution of the ζ potential as a function of pH is shown in Figure 1a for SiOH-functionalized latex particles containing 10 wt % MPS and for pure polystyrene latex particles. These two curves show that the ζ potential is more negative for the functionalized particles than for the unmodified ones. This difference, which is near zero at pH = 2 (isoelectrical point of silica³⁷), increases with pH. These data support the claim that silanol groups are present on the particle surface. The higher the pH, the higher the number of SiO⁻ species, because of the SiOH/SiO⁻ acid/base dissociation equilibrium. At the isoelectrical point of silica, the amounts of negative and positive charges created by the silanol groups are equal, and the difference between unmodified and modified particles becomes zero. The surface potential is still negative at this point because of the presence of anchored sulfate groups of initiator residues.

The ζ potential should also be a function of the MPS concentration because more silanol groups are incorporated in the functionalized particles as the MPS content

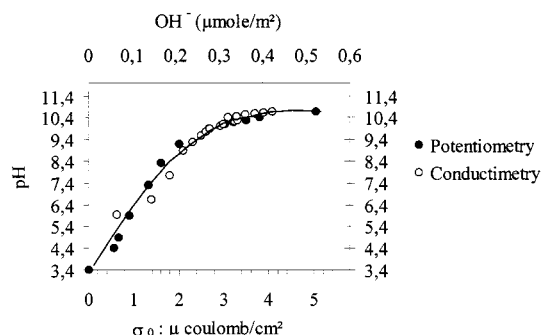


Figure 2. Relationship between the pH and σ_0 determined by potentiometric and conductometric titrations. MPS: 40 wt % relative to styrene.

Table 2. Surface Charge Density (σ_0) of the SiOH-Functionalized Polystyrene Latex Particles at pH = 10.4 for Different MPS Concentrations

	runs			
	0	1	3	4
[MPS] (wt % to styrene)	0	5.5	20.8	40.4
conductometric titration				
$\mu\text{mol}/\text{m}^2$		0.12	0.18	0.32
$\mu\text{C}/\text{cm}^2$		1.15	1.73	3.1
potentiometric titration				
$\mu\text{mol}/\text{m}^2$	0.12	0.22	0.3	0.39
$\mu\text{C}/\text{cm}^2$	1.15	2.1	2.9	3.7

increases. Figure 1b shows the influence of the MPS concentration on the surface potential. The increase in the ζ potential with an increase in the amount of MPS is consistent with the fact that the higher the MPS concentration is, the higher the amount of silanol groups on the particle surface.

Determination of the PZC. It is essential to know the PZC, which corresponds to the pH at which the surface charge is zero, to subsequently determine σ_0 of the functionalized latex particles by chemical titration because it enables us to accurately know the charge status of the particles surface at any time during the titration. The method used to determine the PZC is described above. The PZC thus measured was found to be equal to 3.4 for run 4, which is on the same order of magnitude as the values usually reported for mineral oxide surfaces.^{38,38} The fact that we could determine a PZC definitely proves the amphoteric character of the surface of the functionalized latexes.

σ_0 . In an initial series of experiments, σ_0 was determined as a function of pH using both acid–base potentiometric and conductometric titrations. As an example, the evolution of σ_0 with pH is illustrated in Figure 2 for 40 wt % MPS (run 4). The two techniques give very similar results, and it was found that σ_0 increases with the pH.

In a second series of experiments, σ_0 was determined for different MPS concentrations at fixed pH. The results are reported in Table 2. As expected, based on electrophoretic measurements, σ_0 increases with increasing amounts of MPS. It is possible that the discrepancy observed between the two sets of data for low MPS concentrations is due to the low σ_0 of the particles and thus underlines the uncertainty of the available analytical methods under these conditions.

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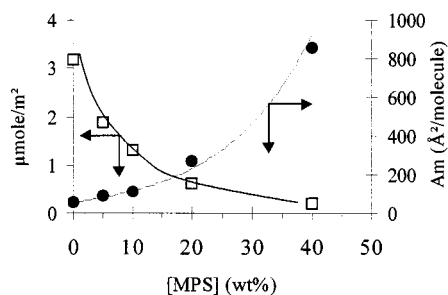


Figure 3. Area per molecule (A_m) and amount of SDS adsorbed on the latex particles surface as a function of the MPS concentration.

Nevertheless, σ_0 of bare polystyrene latex particles, determined using the potentiometric technique (i.e., $1.1 \mu\text{C}/\text{cm}^2$ at $\text{pH} = 10.4$), is in good agreement with σ_0 reported in the literature for polystyrene latex particles stabilized by initiator residues.³⁹ In addition, it is worth pointing out that σ_0 of the SiOH-functionalized latex particles containing 40 wt % MPS is quite close to σ_0 of polystyrene latex particles functionalized by styrene sulfonate comonomer.⁴⁰ Finally, our results are also in good agreement with the titration data given by Bolt on colloidal silica (i.e., $1 \mu\text{mol}/\text{m}^2$).³⁸ The fact that we found fewer surface charges than those on a pure silica surface is presumably due to the presence of styrene units in the copolymers. Indeed, we can estimate that, in run 4, for instance, σ_0 should be of around half the value expected for a pure silica surface considering that the copolymers contain as many styrene units as MPS units. In addition, the data cited above mainly apply to hydrophilic types of silica particles, and it is well-known that the acid–base character of the surface largely depends on the environment of the OH group.

Soap Titrations. The surface polarity of the latex particles after functionalization is directly related to the density of functional groups on their surface. The hydrophilicity of the surface can, therefore, be satisfactorily estimated by measuring the amount of surfactant adsorbed on the particles and determining the surface area occupied by a molecule of the surfactant at saturation. In the current work, SDS was selected as the reference surfactant because its area per molecule is well-known for various polymer surfaces.⁴¹ SDS adsorption was quantified using conductimetry titration as described in the experimental part. The amount of adsorbed surfactant and the corresponding area per molecule (A_m) are plotted as a function of the MPS concentration in Figure 3. As expected, the molecular area of the surfactant at saturation adsorption increases with increasing MPS concentration. The A_m values ranged from 52 \AA^2 for pure polystyrene latex particles (which is in good agreement with the literature data⁴¹) to 857 \AA^2 for the highest MPS concentration. The increase in A_m with increasing MPS content clearly illustrates that the surfactant molecular area is highly dependent on the polarity of the copolymer as reported in the literature.⁴² It is worthwhile to note that the real

fractional amount of MPS incorporated on the surface of the latex particles (with respect to styrene) is higher than the feed composition given in Table 1 because MPS is introduced once 80% of styrene is converted. One can, therefore, determine that, in run 4, for instance, the amount of MPS on the particle surface is approximately 2 times higher than the amount of styrene. Because the surface of the functionalized polystyrene latexes contains a large proportion of MPS, it is not surprising that we obtain high values of A_m . This means that the repulsive forces between the dissociated silanol groups and the surfactant molecule predominate at large MPS concentrations. This result is in agreement with ζ potential measurements and the titration data, which both point to a high density of surface silanol groups for MPS concentrations greater than 10 wt %. It is worth noting that, under these conditions, A_m is significantly higher than the value reported in the literature for poly-(methyl methacrylate) latex particles (i.e., 152 \AA^2),^{41,42} whereas A_m values lower than 152 \AA^2 are obtained for lower MPS concentrations. It, therefore, appears that the surface polarity comes essentially from the dissociated silanol groups and cannot be attributed to the methacrylate function of the silane molecule.

Seeded Growth and Synthesis of Hollow Silica Nanoparticles. Although there exist a number of works in the literature that deal with the coating reaction of polymers with minerals,^{21,29–31,43–50} none of them describe the use of a coupling agent for compatibilization of the inorganic shell with the polymeric core materials. The coating procedures usually reported in the literature generally involve either direct precipitation techniques^{43–46} or the buildup of successive polymer–inorganic layers through electrostatic interactions using the so-called layer-by-layer (LbL) deposition method.^{47–49} The former procedures require the use of stabilizers in order to prevent particles aggregation or to promote coating, and the LbL technique needs purification steps, which are time-consuming. Indeed, separate mineral particles or polymers are formed that must be removed from the suspension after each deposition cycle. To overcome these drawbacks and to provide covalently bonded nanocomposite particles, the SiOH-functionalized polystyrene latexes described above were used as a seed to build up a silica layer on their surface. In a typical procedure, the functionalized latexes were first suspended in ethanol containing 5 wt % of water through dialysis. It is worth pointing out that the modified polymer particles did not agglomerate upon serum replacement regardless of the amount of silanol groups. On the other hand, DLS measurements showed that pure polystyrene latex particles formed aggregates under identical conditions. The colloidal stability of the modified latexes in an alcoholic media could be, there-

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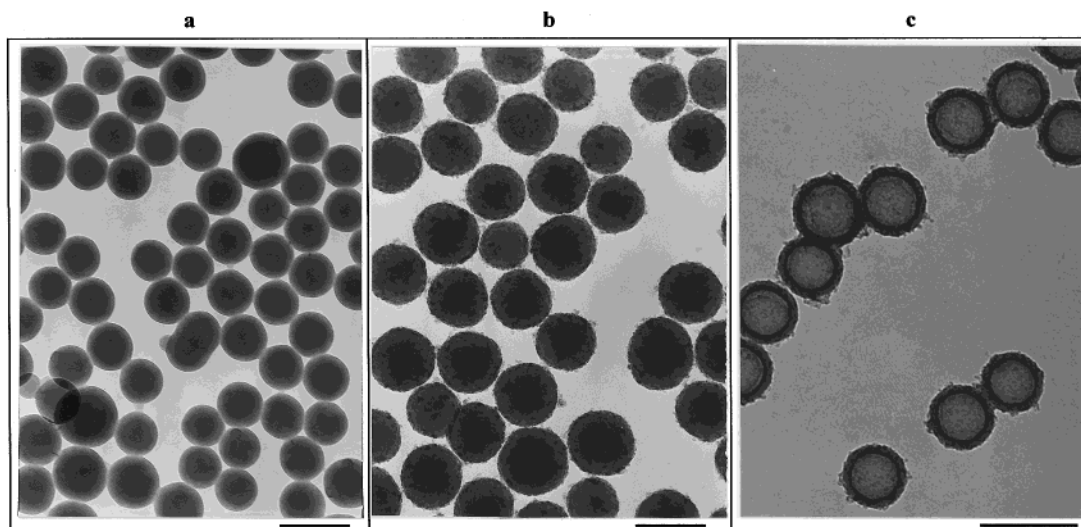


Figure 4. TEM micrographs of (a) SiOH-functionalized latex particles, (b) silica-coated latex particles, and (c) hollow silica nanoparticles.

Table 3. Specific Surface Area, Pore Volume, and Pore Diameter of the Functional Polystyrene Latex Particles, the Silica-Coated Polystyrene Latex Particles, and the Hollow Silica Spheres

	diameter (nm) ^a	specific surface area		pores	
		theoretical (m ² /g) ^b	experimental (m ² /g) ^c	volume (mL/g) ^c	diameter (nm) ^d
SiOH-functionalized latex seed	105	57	20.7	0.16	31.2
silica-coated latex particles	141	29	110.8	0.25	9.2
hollow silica spheres	132	25	141.8	0.38	12.3

^a Determined by TEM. ^b Determined by assuming a spherical shape and a smooth nonporous surface. ^c Calculated using the BET method. ^d Calculated by the BJH method from the desorption curves.

fore, attributed to the silanol groups present on the particle surface. In a second step, TEOS was added to the latex seed suspension in the presence of ammonia following the so-called Stöber process.² Under these conditions, stable nonaggregated suspensions of 20 nm thick silica-coated latex particles were successfully obtained as illustrated by the TEM image in Figure 4. It can be seen from this image that a rough silica coating forms on the latex core and, as shown in Table 3, the particle size simultaneously increases. The most important result of this work is the absence of free silica nanoparticles in the surrounding medium, indicating that the polycondensation reaction exclusively took place at the seed surface. As expected, the attached SiOH functions played the role of anchored groups that promote the formation of a silica layer on the seed surface. We recently reported very similar results during the synthesis of silica-coated polymer particles in emulsion polymerization.⁵⁰ Once again, it is found that the particle morphology is strongly dependent on the nature of the latex core. Another clear advantage of our approach in comparison to existing procedures is that we do not need any surfactant because the functional latex particles are electrostatically stabilized over a large range of pH. In addition, we believe that our method can be easily extended to a variety of polymeric core materials with different chemical compositions and particle sizes. Indeed, preliminary investigations gave promising results in the cases of poly(butyl acrylate) and poly(methyl methacrylate) latexes.¹ Finally, we also showed in a related paper that the inorganic shell thickness can be adjusted by varying the concentration of the sol-gel precursor solution.⁵⁰ The thickness of this

shell should also be dependent on the diameter of the polymer beads.

In a final step, the latex core was removed from the particles by calcination, and the resulting hollow silica spheres were suspended in water with the aid of ultrasound. The particle diameter was found to be very close to the original diameter, indicating that a stable colloidal suspension of nonaggregated hollow silica beads could be readily obtained by that technique (Table 3). The TEM micrograph shown in Figure 4c clearly reveals the hollow structure of the silica beads. In addition, FTIR and chemical analysis confirm that polystyrene has been quantitatively removed from the composite particles.

Porosity Measurements. BET measurements were performed at different stages of the synthesis, i.e., after functionalization, after the coating with silica and after removal of the latex core. The data reported in Table 3 indicate an increase in the specific surface area and in the pore volume after both the coating with silica and the removal of the templating latex core. The significant increase in the surface area upon the formation of the silica layer is principally due to the rough surface of the microspheres, which are composed of small silica aggregates precipitated on the core latex particle and thus do not form a smooth and regular silica coating. The pore volume also significantly increased because of the formation of the nanoporous silica surface, and the pore size decreased from 31 nm to around 9 nm in diameter. The increase in the specific surface area and pore size after calcination lends credence to the claim that the particles are hollow. Indeed, it can be seen that the specific surface area of the hollow silica beads (141.8

m^2/g) corresponds approximately to that of the silica-coated latex particles (i.e., $110.8 \text{ m}^2/\text{g}$) plus that of the template (i.e., $20.7 \text{ m}^2/\text{g}$), while the specific pore volume and mean pore diameter increased because of the formation of a void in the porous silica spheres.

Conclusion

In the current work, polystyrene latex particles carrying silanol groups on their surface were synthesized in emulsion polymerization using MPS as a functional comonomer. ζ potential measurements and soap and surface charge titrations clearly proved that silanol groups were introduced on the surface of the latex particles. The amount of silanol groups at the particle surface was controlled by varying the MPS concentration. σ_0 values between 2 and $3.7 \mu\text{C}/\text{cm}^2$ were found when the MPS content was increased from 5 to 40 wt % (relative to styrene), while the A_m of SDS reached quite high values (typically $857 \text{ \AA}^2/\text{molecules}$) in agreement with the increase in the surface polarity at high MPS levels. Because of the presence of the silanol groups on the particle surface, our system offers several advantages in comparison to previous works. First, it

is worth noting that the functionalization reaction is easy to perform because it involves only one reaction step and one reaction vessel (shot-growth process). Second, the functional groups allow us to create a 20 nm thick hard silica coating without renucleation. Finally, the emulsion polymerization process and the colloidal approach enable us to synthesize calibrated hollow silica beads with controlled pore sizes and diameters of small dimensions. Such materials obviously present promising applications as solid supports for catalysis and in chromatography. Porous particles are also of great interest in paint, coating, and microencapsulation technologies. In addition, the functionalized latexes can be considered as hybrid nanoparticles that could be used in multiple areas of colloidal science where a compatibility between the organic core and a mineral matrix is required.

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